Catalysis Science & Technology

PAPER

View Article Online
View Journal | View Issue

Metal-free B-doped graphene with efficient electrocatalytic activity for hydrogen evolution reaction†

Cite this: Catal. Sci. Technol., 2014, 4, 2023

Bhaskar R. Sathe,[abc] Xiaoxin Zou[ab] and Tewodros Asefa*[ab]

The chemical and physical properties of carbon nanomaterials such as graphene can be tailored by doping their structures with heteroatoms. However, substitutional doping of heteroatoms within carbon nanomaterials requires not only rational synthetic methods but also heteroatom-doping reagents that are easier to employ. Herein we report a facile, wet chemical synthetic method to metal-free, yet catalytically active, B-substituted graphene (B-SuG) by using BH_3-THF—a simple and commercially available borylation reagent. Moreover, we show that the B-doped material (*i.e.*, B-SuG) can serve as an efficient metal-free electrocatalyst for hydrogen evolution reaction (HER). Additionally, we demonstrate that BH_3-THF is a better borylating agent in terms of producing the most effective electrocatalyst than other borylating agents such as $NaBH_4$, $B(OH)_3$, carborane, B_2O_3 and NH_3-BH_3. Compared with the conventional heteroatom-doping methods used for graphene, such as chemical vapor deposition (CVD) and physical vapor deposition (PVD), BH_3-THF certainly also has the added advantage of being more amenable and easier to use. We expect that this work will stimulate future research on synthesis of other innovative and sustainable metal-free materials and catalysts and investigation of the fundamental structure-property relationships in metal-free catalysts/catalysis for renewable energy and other applications.

Received 18th January 2014, Accepted 13th March 2014

DOI: 10.1039/c4cy00075g

www.rsc.org/catalysis

1. Introduction

In the face of declining non-sustainable energy resources such as petroleum and, more importantly, their unabated negative environmental impacts, H_2 has long been considered one of the most promising sources of clean, renewable energy that can meet these challenging problems. However, to make the H_2 economy a reality, efficient electrocatalysts and catalytic technologies that allow sustainable generation of molecular H_2 from water *via* catalytic hydrogen evolution reaction (HER) must be developed.[1–3] Although Pt and related noble metals can efficiently electrocatalyze the reaction, their high cost as well as low abundance in the Earth's crust has been limiting their widespread uses.[4] While the recently discovered HER electrocatalysts based on non-noble metal (*e.g.*, Ni, Fe, Co, and Mo) complexes and their alloys and heterostructures can address some of these issues,[5] such metallic systems have an inherent tendency to undergo oxidation, leaching, and/or sintering, and can thereby lose their catalytic activity under conditions in which HER is often carried out.[5,6] Hence, there has been a burgeoning interest in the development of HER electrocatalysts that are completely metal-free and robust yet efficient and inexpensive.

The discovery of various types of advanced metal-free materials such as graphene, carbon nanotubes, and rubrene that possess interesting properties, akin to some metallic and semiconducting systems,[7–9] has recently given way to research on the potential of such metal-free systems for various applications, including electrocatalysis. Graphene, in particular, has become highly attractive for electrocatalysis because of its superior chemical and thermal stability, excellent electronic and ionic conductivity, and tailorable and useful properties.[10–13] For example, by creating charged groups and defect sites on graphene through modification of the arrangements of its surface carbon atoms, defective graphene (DeG) materials with altered geometric and electronic structure and with surface carbon atoms having low coordination numbers and/or free coordination sites can be produced.[14] When such materials are employed as electrocatalysts, they can induce lower activation barriers or improved adsorption energy to reactants, products, or intermediate species, giving rise to higher catalytic activity and/or selectivity for certain electrocatalytic reactions.[14,15]

[a] Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, NJ 08854, USA. E-mail: tasefa@rci.rutgers.edu
[b] Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, 98 Brett Road, Piscataway, New Jersey 08854, USA
[c] Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Maharashtra 431004, India

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4cy00075g